## **BEST AVAILABLE COPY**



Europäisches Patentamt

**European Patent Office** 

Office européen des brevets



EP 0 766 080 A1 (11)

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

02.04.1997 Bulletin 1997/14

(51) Int. Cl.<sup>6</sup>: **G01N 21/39**, F23N 5/08

(21) Application number: 95830401.6

(22) Date of filing: 29.09.1995

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IE IT LI LUMC NL PT SE

Designated Extension States:

LT LV SI

(71) Applicant: FINMECCANICA S.p.A. AZIENDA **ANSALDO** 

I-20122 Milano (IT)

(72) Inventors:

Calabro', Bruno I-16161 Genova (IT)

· Frontini, Luis I-16149 Genova (IT)

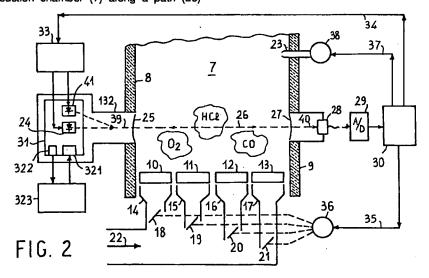
 Repetto, Francesco I-16161 Cogoleto(Genova) (IT)

(74) Representative: Falcetti, Carlo et al c/o JACOBACCI & PERANI S.p.A. Via Visconti di Modrone, 7 20122 Milano (IT)

#### (54)System and method for monitoring combustion and pollutants by means of laser diodes

(57)A system for monitoring combustion and pollutants developed in a combustion chamber (7) comprising at least one longitudinal single mode laser diode (24) emitting a beam of electromagnetic radiation with a frequency modulated around the resonance frequency of a specific spectral absorption line of a component of the combustion gases, means (39) for directing the beam into the combustion chamber (7) along a path (26)

through the combustion gases to a radiation sensor (28) and processing means (29, 30) connected to the sensor (28) in order to identify the temperature of the combustion gases and the concentration of the component with the specific absorption line by the measurement of the intensity of radiation transmitted at various frequencies in a region surrounding the resonance frequency.



35

#### Description

## FIELD OF THE INVENTION

The present invention relates to a system and a method for measuring the temperature and the concentration of O<sub>2</sub>, CO, HCl and other chemical species contained in the flames and in the combustion fumes developed in thermal plants and incineration plants.

1

The purpose of the measurement is to monitor the combustion/incineration and/or the hot neutralization of the acid substances resulting from the incineration or combustion.

Although the main field of application of the system is that of waste incineration plants, the system can also be used in thermal plants supplied with coal, hydrocarbons or gases resulting from the gasification and pyrolysis of waste, biomasses or other combustibles.

The need to provide systems for measuring and controlling combustion results from the ever greater care taken both in optimizing the combustion process and in controlling pollutant emissions. The use of fuels which are non-homogeneous in form and chemical characteristics, such as urban waste in particular, increases these problems.

### STATE OF THE ART

It is in fact known that, in order to achieve complete combustion of the fuel it is necessary to provide an excess of air relative to the stoichiometric combustion ratio, which excess depends upon the physical characteristics of the fuel but reduces the heat yield. Moreover, the excess of air favours the development of toxic substances such as  $NO_X$  at high temperatures.

The main parameter which is generally used for monitoring combustion is the temperature in the combustion chamber which is measured with the use of optical pyrometers or video cameras sensitive in the infrared and visible ranges. These systems have quick enough responses to permit automatic regulation which, however, remains subject to considerable uncertainty. Complementary monitoring of the composition of the combustion fumes is also carried out by the withdrawal, cooling and analysis of suitable samples in suitable analyzers (ORSAT equipment and the like).

The analysis process is relatively slow and is not suitable for controlling combustion if heterogeneous fuels such as urban waste with greatly variable characteristics are used.

Moreover, the standardization of the samples may bring about a considerable difference between the composition of the combustion fumes in their actual situation and the samples analyzed.

Absorption spectroscopy systems have also been proposed for detecting the concentration of some particular pollutant substances in the combustion fumes emerging from the plant.

For example, the document EP-0084726 describes

a system for detecting the concentration of NH<sub>3</sub> in the fumes of a plant using two CO<sub>2</sub> lasers to generate two beams of monochromatic light with a wavelength which is spectrally selectively absorbed by NH<sub>3</sub> and with a wavelength which is not selectively absorbed, respectively.

The two beams pass through the fumes of the plant along the same active path and the intensity transmitted is detected by sensors which provide an indication of the spectrally selective absorbtion brought by NH<sub>3</sub> by means of the difference, corrected in dependence on any different intensity of emission of the two lasers, and cleaned of noise and non spectrally-selective absorption due to the system, to blown ash and the like.

Since absorbtion depends on temperature as well as concentration, a thermoelectric sensor enables the absorption measurement to be corrected according to temperature, and the concentration of NH<sub>3</sub> in the fumes to be found.

The problem of the absorption depending on the composition of the fumes, that is, of the partial pressures of the various chemical species present is avoided by the assumption that some chemical species are present in concentrations which are variable within predetermined limits, which limits the uncertainty of the measurement.

The document EP-0318752 describes a system similar to that referred to above in which a single  $CO_2$  laser is operated to generate, at distinct time intervals, monochromatic light with two wavelengths which are spectrally selectively absorbed and are not absorbed by  $NH_3$ , respectively.

Although the systems described are effective for identifying and measuring the concentration of a single chemical species, even in hot fumes, they are limited in their application to cases in which the composition of the fumes is only slightly variable but, on the other hand, are not suitable for applications in which the composition is greatly variable, as in the case of incineration plants.

Moreover, they require a temperature measurement carried out with thermometric probes, the precision of the concentration measurement depending on the precision and sensitivity of this temperature measurement which is in any case limited.

"In situ" use for detecting several chemical species would be of prohibitive complexity, bulk and cost owing to the need to provide cooling systems, insulation from mechanical and sound vibrations, and continuous control and adjustment of the working point for a plurality of gas lasers which are intrinsically expensive, bulky and require adequate support instrumentation which is also bulky and expensive.

#### SUMMARY OF THE INVENTION

These limitations are overcome by the monitoring system of the present invention which is simple, compact and extremely precise and can measure the con-

35

45

50

55

fumes of which it forms part, by means of the width of the Doppler component of the line.

centration of a chemical species and its temperature with the use of a single source of monochromatic light such as a longitudinal single mode laser diode and, with the use of several sources of monochromatic light, can define a map of fume temperatures in various regions of a combustion chamber and can precisely measure concentrations of several chemical species of interest.

This information is available within very short measurement times of less than 100 msec, enabling combustion to be optimized by the regulation, which may be automatic, of the principal parameters such as primary air, secondary air, and others (such as the sectorizing of the quantity of air in grating furnaces) permitting better control of the most critical regions, reducing excess air, unburnt substances and their contribution to the formation of pollutants to a minimum, optimizing the consumption of reagents used to destroy acid substances such as HCl, HBr, SO<sub>2</sub>, HF and others, and homogenizing the temperature of the fumes before they pass through the recovery boiler.

The intrinsic advantages of the system are:

- high sensitivity and precision (1ppm, and 1°C)
- speed of measurement (100 ms)
- very wide field of measurement
- absence of moving parts and chemical reagents or catalysts (which are necessary, for example, in conventional analysis equipment)
- minimal bulk and ease of transportation and installation,
- low cost
- good reliability and zero maintenance.

These results are achieved by a monitoring system according to the invention in which one or more longitudinal single mode laser diodes emit a beam of monochromatic light each with a wavelength close to that of a preselected absorption line specific to a chemical species to be identified and measured quantitatively.

The monochromatic light beam or beams, guided optically by mirrors or optical fibres if necessary, penetrate the combustion chamber through self-cleaning optical windows, pass through the fumes and are collected by one or more sensors which send signals to a processing and control station of the system, which may be a remote station.

The processing and control station imposes on the laser diodes a periodic modulation of the wavelength emitted by the diodes sufficient to scan the entire amplitude of the preselected absorption line so as to detect the complete shape of the absorption line.

From an analysis of the shape of the absorption line carried out by "fitting" procedures, the processing station can discriminate between the "Doppler" or temperature component of the shape of the line and the other components and can identify the concentration of the chemical species by means of the maximum intensity of the Doppler absorption component, and also the temperature of the chemical species and, naturally, of the

Unlike known measurement methods which are based on the recognition of two absorptions with different wavelengths, the measurement method, which is based on a "fitting" operation and hence analysis of the complete shape of an absorption line, is made possible by the use of longitudinal single mode laser diodes which have a wide tuning range of the order of tens of GHz associated with a very narrow line width emitted of the order of one MHz which, can be further reduced by suitable measures.

The frequency emitted by the laser diodes can easily be varied and controlled by the modulation of the supply current and the temperature of the working point can easily be stabilized by simple and compact thermostatic systems.

The devices can also be isolated easily and cheaply from noise and vibrations which are always present to a considerable extent in combustion plants.

#### SHORT DESCRIPTION OF THE DRAWINGS

The characteristics and advantages of the system and method of the present invention will become clearer from the following description and from the appended drawings, in which:

- Figure 1 shows qualitatively in a graph of absorption (A)/frequency f (or pulsation  $\omega$ ) the various components which determine the shape of a spectral absorption line,

Figure 2 shows schematically a preferred embodiment of the monitoring system according to the present invention, applied to a incinerator with a grating.

## **DETAILED DESCRIPTION**

Before describing the monitoring system and the method of the present invention, it is appropriate to set out some considerations of a general character beforehand.

It is known that the absorption lines of an absorption spectrum for a predetermined chemical species are not actually lines corresponding to a predetermined frequency but absorption bands extending around a predetermined frequency or resonance frequency with a shape and width which depends on various factors.

Monitoring the "natural" broadening which leads to a homogeneous band width of equal amplitude of the order of hundreds of Hz, the factors which contribute most to the shape and width of the absorption band are:

## 1) Doppler broadening:

In a gas, the molecules have different velocities with different orientations relative to a common reference

such as a light source.

The velocities have a Gaussian distribution depending on the gas temperature.

This distribution causes, by the Doppler effect, a corresponding distribution in the frequencies at which 5 the molecules or atoms can absorb the photons.

The absorption lines therefore assume a bell-like Gaussian shape the width of which is greater the higher the temperature.

The shape of the absorption line is described by the  $\phantom{-}$  10 function

I + lo exp [- 
$$\frac{\text{M.C}^2.\Delta\omega^2}{2\text{K}_B \text{ T} \omega_2}$$
]

where

C = the speed of light  $\Delta \omega$  = the deviation from the resonance fre-

quency expressed in pulsations

 $(\Delta\omega = 2 \Pi \Delta f).$ 

 $\begin{array}{lll} K_B & = \text{the Boltzman constant} \\ T & \text{is the absolute temperature} \\ \omega & \text{is the independent variable} \\ M & \text{is the molecular mass} \end{array}$ 

From this function it is easy to derive the width of the absorption line, which is proportional to the square root of the absolute temperature and, although proportionally variable with the frequency and dependent on the molecular mass, at ambient temperature and in the range of absorption frequencies corresponding to wavelengths between 1 and 2  $\mu$ m, is of the order of hundreds of MHz and much greater than the natural broadening.

For example, in the range of wavelengths between 1 and 2  $\mu m$  NH $_3$  and H $_2$ O molecules have Doppler widths of 400 and 150 MHz respectively at ambient temperature and at the respective resonance frequencies and these are approximately doubled at a temperature of 800-900°C.

### 2) Broadening owing to "collision" or to "pressure":

When the molecules of a gas or of a mixture of gases move, their motion brings them towards one another and they interact causing a change in their energy and vibration states with an equal probability that the molecules will assume an energy level which differs from that before the collision by any value between  $\pm$  E where E depends upon the pressure, the temperature and other factors; this causes a homogeneous broadening of the absorption line which, by this effect alone, that is, in the absence of a DOPPLER effect, assumes the shape of an equi-absorption band, or Lorenztian function centred on the resonance frequency and having an amplitude H defined by H =  $1/\Delta v_{\rm L}$ 

and a width  $\Delta v_i$  defined in short by the equation

$$\Delta V_{L} = K(T, P_{1}, P_{2} ... P_{N}) . P$$

where Δ<sub>V</sub> is the broadening owing to collisions expressed as wavelength,

K(T,  $P_1$ ,  $P_2$  ...  $P_N$ ) is a variable coefficient depending upon the temperature T and the partial pressures  $P_1$  ...  $P_N$  of the various chemical species constituting the gaseous mixture and P is the total pressure.

This further broadening is combined with the Doppler contribution (on all of the lines which make up the absorption spectrum determined by the Doppler effect) and the resulting effect on the shape of the absorption line is that it assumes a Voight profile, that is, a profile of the convolution or integral product of the Gaussian function and of the Lorentzian function.

Figure 1 shows qualitatively in a graph of absorbency Afrequency the natural shape of an absorption line 1 centred on a resonance frequency f<sub>0</sub>, the shape resulting from the Doppler effect alone (Gaussian curve 2), the shape resulting from the broadening owing to pressure alone (Lorentzian curve 3) and the Voight profile 4 resulting from the accumulation of the effects.

As can be seen, the absorbency of the absorption line is considerably attenuated at its peak value and is spread more uniformly.

The broadening owing to collisions dominates at atmospheric pressure where it is of the order of 1 GHz and more, that is, of an order of magnitude greater than the Doppler contribution, whereas at low pressures of the order of 5-10 Torr there is practically only the Doppler contribution.

Whilst the Doppler broadening for a given chemical species and resonance frequency depends solely on temperature, the broadening owing to collisions depends not only upon the pressure but also, and to a considerable extent, on the temperature and the composition of the gaseous mixture.

Since the peak absorption value depends on the broadening owing to collisions (the areas 5 and 6 of Figure 1 should be equal) it is virtually impossible to identify the concentration of a chemical species by an absorption peak measurement in the presence of other chemical species without knowing their concentrations, and hence partial pressures, and the temperature.

It is clear, however, that if the entire shape of the Voight profile (or at least half of it) can be detected it is possible, by analytical processing or fitting methods to identify the equation of the particular Gaussian curve which, combined with a Lorentzian curve, produces the Voight profile shape detected.

The identification of this Gaussian curve defines its width and its amplitude (peak value).

By the measurement of the width, which is due solely to the Doppler contribution and therefore for a given resonance frequency and chemical species depends solely on temperature, it is possible to calculate the temperature.

The amplitude, on the other hand provides a measurement of the absorbency A of the chemical species, cleaned of the broadening effects due to pressure.

The absorbency A thus corrected enables, by

20

means of the known Beer Lambert law which links transmissivity to concentration:

$$I = I_0.e^{-\sigma(\omega)NL}$$

where

l <sub>0</sub> =	intensity of incident radiation
.u - I =	intensity of radiation transmitted
σ(ω) =	specific parameter of the chemical
	species considered, variable with frequency ( $f=\omega/2\Pi$ )
N =	concentration
L=	length of absorption path.

enables as said the concentration N of the chemical species monitored to be determined.

In fact A =  $(I_0 - I)/I_0 = 1 - e^{\sigma(\omega)NL}$ 

This measurement, which is based on the recognition of the shape of the absorption spectrum, is independent of the pressure and composition and minimizes errors resulting from noise and interference which, to have a significant effect on the accumulation of the measurements, would have to have a Gaussian distribution in the spectrum of frequencies examined.

In order to implement this method in an industrial context, such as an incineration plant or a thermal plant, it is necessary to have available one or more sources of monochromatic light of extreme spectral purity and with a frequency which is adjustable continuously and repetitively throughout the range of frequencies affected by the Voight profile relating to an absorption line to be analyzed. As already stated, the spectral width of the emission should be of the order of a few MHz or less and the frequency adjustability should extend to a few GHz. The light source should have an intensity which is known even if it is not necessarily constant at the various scanning frequencies and should be insensitive to vibrations and noise.

The structures for the installation of the light source and the control equipment should be simple, cheap and compact.

These requisites, together with those of good reliability and compactness are satisfied by laser diodes emitting in longitudinal single mode, of the type used for telecommunications.

Laser diodes with emission in the red wavelength band (0.6-0.7  $\mu$ m; InGaP diodes) and in the near infrared bands (0.7-0.9  $\mu$ m: GaAlAs diodes; 1-2  $\mu$ m: InGaAsP diodes) are already on the market.

The emission spectra of these diodes cover a frequency band in which secondary absorption bands or lines of the chemical species of interest in the monitoring of concentrations of fumes are present and which are therefore less intense than the fundamental bands, possibly by two orders of magnitude.

This fact, which considerably limits the sensitivity of measurements effected by conventional techniques does not, however, substantially adversely affect the precision achievable by the method described.

Figure 2 shows, in generally schematic form, a system for monitoring the temperature of fumes applied to an incineration plant, for example, of the type with a grating.

The incineration plant comprises a combustion chamber 7 surrounded by refractory walls 8, 9, at the base of which a sectorized grating 10, 11, 12, 13 transports the fuel constituted by waste to be incinerated.

Air inlet ducts 14, 15, 16, 17 choked by regulating shutters 18, 19, 20, 21 admit a suitable flow of combustion air 22 to the combustion chamber 7 through the grating and the bed of waste.

As a result of the combustion, acid substances, particularly HCl, are developed in the fumes and, in order to destroy these, a suitable flow of a basic substance, preferably CaCO<sub>3</sub> powder, is admitted to the combustion chamber, for example as described in European patent application EP-A-0605041.

The admission takes place by means of suitable nozzles 23.

The temperature of the fumes is normally monitored by thermometric probes, the indications of which are used by regulation systems to act appropriately on the shutters 18, ...21 and/or to activate auxiliary burners, not shown, so as to keep the temperature of the fumes within a predetermined range, for example 850-950°C.

It is also desirable to measure the concentration of HCl in the fumes in order to regulate the flow of basic substance appropriately so as to achieve an optimal destruction of HCl with the minimum consumption of basic substance.

In order to measure the HCl concentration and the temperature jointly, the incineration plant is equipped with a monitoring and regulation system which comprises a laser diode 24 with longitudinal single mode emission which sends a monochromatic radiation beam into the combustion chamber 7 through an optical window 25, which is preferably self-cleaning, formed in the wall 8 of the furnace.

The beam passes through the fumes along an absorption path 26 and, through an optical window 27 formed in the wall 8 opposite the wall 9, strikes a radiation sensor 28 spectrally sensitive to the radiation emitted by the diode 24.

The analog signal emitted by the sensor 28 is sent to an A/D converter 29 and from there to a processing and control unit 30.

To avoid direct exposure of the diode 24 and the sensor 28 to the temperatures of the furnace, these may also be installed in positions remote from the furnace walls and the light beam may be conveyed from the diode 24 to the optical window 25 by means of an optical guide 39, in air, inert gas or optical fibre and, from the optical window 27 to the sensor 28 by equivalent means 40.

Alternatively, to reduce the number of passages through the furnace walls, the optical window 27 may consist of a mirror which sends the incident beam back

towards the optical window 25 and through it to the sensor 28.

The length of the optical path is thus doubled and the sensitivity of the measurement system increased.

This can be further increased, within certain limits, 5 by multiple reflections.

Since the spectral purity of the radiation emitted by the diode 24 is affected by sound vibrations of both low and high frequency, the diode 24 is fitted on an antivibration support 31 enclosed in a suitable housing 132.

The support 31 which is advantageously of material with high thermal conductivity such as copper, is kept at a temperature controlled precisely by a temperature regulation system comprising a Peltier cell 321 connected to the support, a resistive temperature-measurement bridge 322 and a supply 323 for the Peltier cell, controlled by feedback of the temperature measurement.

A controlled supply 33 supplies the diode 24 with a predetermined current supply variable according to predetermined periodic laws, for example, with periodic saw-tooth, triangular or even sinusoidal slopes with periodicity of the order of 10-20 ms corresponding to a frequency of 50-100 Hz.

As is known, the intensity and frequency of the radiation emitted by a laser diode vary in dependence on the supply current, in known manner.

With a constant temperature ensured by the temperature control system, it is therefore possible to correlate a predetermined emission intensity lo and a predetermined wavelength of the radiation emitted with each predetermined supply current.

There is no difficulty in obtaining continuous excursion ranges of the wavelength of radiation emitted of the order of 10 GHz and even more from a longitudinal single mode laser diode such as DFB (distributed feedback) or DBF (distributed Bragg reflector) diodes.

The average emission frequency of the diode 24 is selected so as to correspond to a spectral absorption line of a chemical species to be determined (in the example described, HCI) which is advantageously distant from other spectral absorption lines of the same chemical species or of other chemical species which may be present in the fumes, such as CO, CO<sub>2</sub>, H<sub>2</sub>O, SO, N, O<sub>2</sub> to prevent interference between adjacent absorption lines. Purely by way of example, in the case of HCI, the absorption line corresponding to the second overtone at 1207.9 nm may be selected.

As already stated, by varying the emission frequency of the laser continuously around the wavelength of 1207.9 nm it is possible to detect, by means of the sensor 28, the shape of the absorption line throughout a region surrounding the nominal wavelength corresponding to the resonance frequency selected.

The signal emitted by the sensor 28 is sampled and converted into digital form with a suitable period, for example 10 µs, by an A/D converter 29. The binary code output by the converter 29, which is indicative of the transmissivity of the optical path 26, is sent to the

processing unit 30.

The unit 30 preferably but not necessarily sends suitable synchronization signals to the regulation system 33 by means of wires 34 so that the emission intensity of the diode 24 at the time, which is variable with the supply current, is known.

The data received in chronological succession by the processing unit 30 via the A/D converter 29 are corrected by the unit 30 in dependence on the variable intensity emitted and are stored. They are representative of the absorption detected point by point throughout the band of the absorption line.

If, as stated, the scanning takes place in 10 ms and the sampling of the signal has a periodicity of 10  $\mu$ s, 1000 measurements which precisely describe the shape of the absorption line are collected and stored.

By an examination of the data collected, the processing unit 30, suitably programmed, can identify by known "fitting" techniques or even differential analysis, the Gaussian component of the shape of the absorption line detected and hence the temperature of the fumes and the concentration of HCl along the optical path as well as the background absorption or noise of the detection system.

Unlike measurement systems which reduce random measurement errors, but not systematic errors, to a minimum by repetition of the measurement under the same conditions, the method implemented also minimizes systematic errors.

It is possible to establish an analogy between the method implemented and holographic techniques; a hologram of an object is the description of the image of an object by a representation of each point of the image distributed at each point of the hologram according to predetermined optical laws.

It is possible, by the same optical laws, to reconstruct the initial image, but a single error occurring in the reconstruction in the formation of a point of the hologram, like the accumulation of single errors, has a negligible effect on the image reconstructed.

These affect the reconstructed image only if the errors are distributed according to a law which interferes with the optical laws used in the generation and reconstruction of the hologram.

In the present case, the shape of the absorption line is determined according to physical laws such as the convolution of a Gaussian curve and of a Lorentzian curve and, by the application of these laws, it is possible to derive from the plurality of measurements the Gaussian component and its characteristics parameters even if the single measurements are affected by errors. The only errors which affect the reconstruction of the Gaussian curve are errors distributed, in dependence on the wavelength, by Gaussian laws; that is not the case for the measurement errors due to noise or to sensitivity limits of the detection system.

It is therefore clear that, after a period for the collection of data which, by way of indication may be 10 ms, and a processing time which is also very short and of the order of a few tens of milliseconds, the processing unit 30 can provide a precise joint measurement of temperature and concentration even with the use simply of a personal computer with limited calculating power.

By comparing the temperature detected with a desired temperature, the processing unit 30 can generate an error signal (analog or digital) which is transferred by means of wires 35 to a regulation member 36 for the opening/closure of the shutters 18 ... 21 and/or the control of auxiliary burners.

The indication of the HCl concentration can be converted by suitable laws into a control signal sent through wires 37 to a member 38 for regulating the flow of basic substance which is admitted to the combustion chamber.

Clearly, with the use of a plurality of laser diodes such as 24, 41 operating at different frequencies, each linked with an absorption line of a different chemical species, it is possible to identify the concentrations of various chemical species of interest, such as CO,  $O_2$ ,  $SO_2$ ,  $NH_3$ .

As shown in Figure 2, the radiation emitted by the various diodes can be conveyed along the same optical path or along adjacent optical paths through the same optical input and output windows so as to reduce the number of penetrations to a minimum.

The recognition can be carried out by a plurality of sensors such as 28, each associated with a diode, or even by a single wide-spectrum detection sensor.

In this second case, electro-optical switches or rotating mechanical obturation devices enable the radiation emitted by each diode to pass through the window 25 in different and successive time periods.

The use of a plurality of diodes and sensors arranged so as to form a plurality of optical paths in the combustion chamber, which are at least partially distinct and possibly intersecting, permits the detection of the concentration of several chemical species and, at the same time, a temperature map of the combustion chamber by means of which to regulate the combustion by selective action on the primary air control shutters and/or on a plurality of auxiliary burners, or even on shutters for deflecting the fumes output by the combustion chamber to optimize the distribution of the thermal flow through the recovery boiler.

In this case it is also possible to make use of a number of sensors smaller than the number of laser diodes, the various transit paths which are made to converge on the sensors being enabled selectively by means of shutters.

It is also clear that, although the identification method described is preferable owing to its precision and immunity to interference, less precise analytical methods may be used.

For example, if the changes in concentration of the various components of the fumes have a negligible effect on the broadening of the absorption line and compensate for one another and the width of the absorption line can therefore be considered to depend solely on the

temperature, it is possible, by a frequency scanning method, to identify the band width and to derive the temperature therefrom, possibly with the measurement of the pressure in the combustion chamber if this differs significantly from atmospheric pressure.

It is then possible, with the measurement approximations to which the cited document EP-0084726 refers, to identify the concentration of the chemical species purely on the basis of the measurement of the absorption peak.

In particular, in the case of a monitoring system in which a plurality of laser diodes is used, in order to recognize the concentration of different chemical species, if temperature mapping is not required, all of the diodes except one may operate at frequencies linked with the respective absorption lines in order to measure solely the amplitude of the absorption peak and possibly the zero level or background absorption level.

This latter indication, with the necessary corrections due to the possible difference in intensity may be supplied by the laser diode which has the task of measuring the temperature by frequency scanning.

#### Claims

- A system for monitoring a combustion process with the development of pollutant substances in the combustion fumes in a combustion chamber (7), comprising:
  - at least one longitudinal single mode laser diode (24) emitting radiation at a wavelength corresponding to that of a specific spectral absorption line of a predetermined chemical species.
  - modulation means (33) for periodically modulating the wavelength of radiation emitted in a region surrounding that of the absorption line,
  - conveyor means (39) for directing the radiation along a transit path (26) through the combustion chamber (7),
  - collector means (40) for receiving a fraction of the radiation which has not been absorbed along the transit path (26) and for conveying it to detection means (28) comprising at least one radiation sensor (28), the radiation sensor generating a signal correlated to the intensity of the radiation fraction, and
  - processing means (29, 30) connected to the detection means (28) for identifying jointly, in dependence on the signal received by the detection means (28) and sampled at successive moments, the temperature of the combustion fumes passed through along the transit path and the concentration of the predeter-

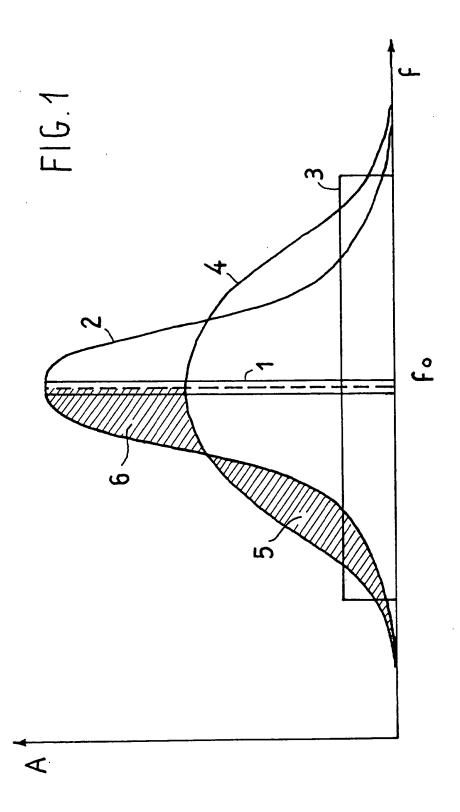
25

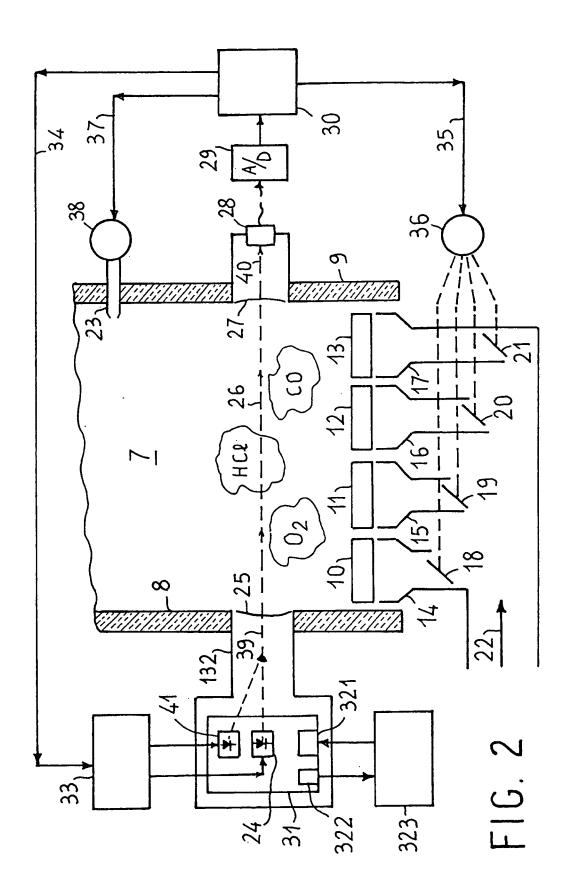
mined chemical species.

- A monitoring system according to Claim 1, comprising regulation means (36) connected to the processing means (30) for controlling a parameter of the combustion process in dependence on the temperature identified by the processing means (30).
- A monitoring system according to Claim 1, comprising regulation means (38) connected to the processing means (30) for controlling a parameter of the combustion process in dependence on the concentration identified by the processing means.
- 4. A monitoring system according to Claim 1, comprising first regulation means (36) connected to the processing means (30) for controlling a first parameter of the combustion process in dependence on the temperature identified by the processing means (30) and second regulation means (39) connected to the processing means (30) for controlling a second parameter of the combustion process in dependence on the concentration identified by the processing means.
- A monitoring system according to Claim 1, comprising at least one second laser diode (41) emitting radiation at a wavelength corresponding to that of a specific spectral absorption line of a second predetermined chemical species, means (39) for directing the radiation emitted by the second laser diode into the combustion chamber and detector means (28) for generating a second signal, correlated to the intensity of the fraction of radiation emitted by the second laser diode which is not absorbed in the combustion chamber, the second signal being supplied as an input to the processing means (29, 30) and processed by said processing means to identify the concentration of the second chemical species in the combustion chamber.
- A monitoring system according to Claim 1, comprising a thermally conductive anti-vibration support
   (31) for the at least one laser diode (24) and means
   45
   (321, 322, 323) with Peltier cells (321) for regulating the temperature of the anti-vibration support.
- 7. A monitoring system according to Claim 5, comprising an anti-vibration support (31) for the at least one longitudinal single mode laser diode (24) and the second laser diode (41) and means (321, 322, 323) with Peltier cells (321) for regulating the temperature of the anti-vibration support.
- A method for the joint determination of temperature and concentration of a chemical species in a mixture of gases, consisting of

- passing, through a volume of the mixture of gases, a beam of electromagnetic radiation of known intensity and high spectral purity with a frequency modulated around the frequency of a specific absorption line of the chemical species, the absorption line comprising a Gaussian component,
- measuring the absorption of the radiation in the volume at the various frequencies in order to derive the spectral distribution of the absorption.
- identifying the Gaussian component of the spectral distribution, the corresponding temperature determined by the Gaussian component, and the concentration of the chemical species.

8







## **EUROPEAN SEARCH REPORT**

Application Number EP 95 83 0401

Category	Citation of document with it of relevant pa	ndication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)		
Y	APPLIED OPTICS, vol. 32, no. 30, 20 US, pages 6104-6116, XP M. P. ARROYO ET AL. * page 6104 - page		1-8	G01N21/39 F23N5/08		
Y	OPTICS LETTERS, vol. 19, no. 22, 15 US, pages 1900-1902, XP D. S. BAER ET AL. * the whole documen		1-8			
Y	UND ENERGIETECHNIK)	TIN GMBH FÜR UMWELT- - line 48; claims 6,7	2			
Y	UND ENERGIETECHNIK)	TIN GMBH FÜR UMWELT- - column 8, line 25 *	3,4	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
Υ	pages 304-311, XP 0 F. WITTGREFE ET AL.	1 1991 BRISTOL GB, 00227786	6,7 F23N F23G F23J			
Y	APPLIED OPTICS, vol. 29, no. 33, 20 US, pages 4860-4872, XFA. ARNOLD ET AL. * abstract * page 4862 *	November 1990 NEW YORK 0000165580	6,7			
	The present search report has b	<u> </u>				
Place of search BERLIN		Date of completion of the search 14 March 1996	Br	rison, O		
Y:paz do A:tex O:no	CATEGORY OF CITED DOCUME ticularly relevant if taken alone ticularly relevant if combined with an ament of the same category hnological background n-written disclusure ermediate document	NTS T: theory or princ E: earlier patent of after the filing other D: document cited L: document cited	iple underlying to locument, but pr date I in the applicat for other reason	the invention ablished on, or		



## **EUROPEAN SEARCH REPORT**

Application Number EP 95 83 0401

Category	Citation of document with ind of relevant pass		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)
A	US-A-5 252 060 (J. T * column 7; figure 1	. MCKINNON ET AL.)	1	
A,D	EP-A-0 084 726 (EXXO ENGINEERING CO.) * abstract *		1,8	
		<del></del>		
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	The present search report has be	en drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	BERLIN	14 March 1996		ison, O
BERLIN  CATEGORY OF CITED DOCUMENTS  X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		TS T: theory or pr E: earlier pater after the fill ther D: document of L: document of	inciple underlying that document, but pulling date ited in the application ted for other reasons	e invention blished on, or

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

# **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:
☐ BLACK BORDERS
☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
FADED TEXT OR DRAWING
☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
☐ SKEWED/SLANTED IMAGES
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
☐ GRAY SCALE DOCUMENTS
☐ LINES OR MARKS ON ORIGINAL DOCUMENT
REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
Потить

# IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.





# United States Patent and Trademark Office

UNITED STATES DEPARTMENT OF COMMERCE United States Patent and Trademark Office Address: COMMISSIONER FOR PATENTS P.O. Box 1450 Alexandria, Virginia 22313-1450 www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/543,288	07/25/2005	Andrew D Sappey	ZOLO.37/PCT-US 2065	
25871	7590 09/05/2006		EXAMINER	
	& BRATSCHUN L.L.C	· ·	KIM, EL	LEN E
1745 SHEA C SUITE 330	CENTER DRIVE		ART UNIT	PAPER NUMBER
HIGHLAND	HIGHLANDS RANCH, CO 80129		2874	
			DATE MAILED: 09/05/2006	5

Please find below and/or attached an Office communication concerning this application or proceeding.

	Application No.	Applicant(s)	
	10/543,288	SAPPEY ET AL.	
Office Action Summary	Examiner	Art Unit	
	Ellen Kim	2874	
The MAILING DATE of this communication app Period for Reply	ears on the cover sheet with the c	orrespondence address	
A SHORTENED STATUTORY PERIOD FOR REPLY WHICHEVER IS LONGER, FROM THE MAILING DA  - Extensions of time may be available under the provisions of 37 CFR 1.13 after SIX (6) MONTHS from the mailing date of this communication.  - If NO period for reply is specified above, the maximum statutory period way failure to reply within the set or extended period for reply will, by statute, Any reply received by the Office later than three months after the mailing earned patent term adjustment. See 37 CFR 1.704(b).	ATE OF THIS COMMUNICATION 36(a). In no event, however, may a reply be tim rill apply and will expire SIX (6) MONTHS from cause the application to become ABANDONE	l. ely filed the mailing date of this communication. D (35 U.S.C. § 133).	
Status			
3) Since this application is in condition for allowant closed in accordance with the practice under E	action is non-final. nce except for formal matters, pro		
Disposition of Claims			
4)	vn from consideration.  ected to. r election requirement.  r. epted or b) objected to by the Edrawing(s) be held in abeyance. See on is required if the drawing(s) is obj	37 CFR 1.85(a). ected to. See 37 CFR 1.121(d).	
Priority under 35 U.S.C. § 119			
<ul> <li>12) Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).</li> <li>a) All b) Some * c) None of:</li> <li>1. Certified copies of the priority documents have been received.</li> <li>2. Certified copies of the priority documents have been received in Application No</li> <li>3. Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).</li> <li>* See the attached detailed Office action for a list of the certified copies not received.</li> </ul>			
Attachment(s)  1) Notice of References Cited (PTO-892)  2) Notice of Draftsperson's Patent Drawing Review (PTO-948)  3) Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)  Paper No(s)/Mail Date 9/05, 7/05.	4)  Interview Summary Paper No(s)/Mail Da 5)  Notice of Informal Pa		

Application/Control Number: 10/543,288

Art Unit: 2874

## **DETAILED ACTION**

This is responsive to Applicant's amendment filed on 7/21/05.

Claims 1-32 are examined in this application.

## Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless -

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1-6, 20, and 25 are rejected under 35 U.S.C. 102(b) as being clearly anticipated by Anjan et al [USPAT 5,042,905].

Anjan et al disclose a sensing apparatus comprising:

more than one diode laser [102 in fig. 7];

a multiplexer 104;

a pitch optic and a catch optic [24, 26 in fig. 3];

a process chamber 38;

a demultiplexer [see column 6, lines 3-41]; and

a detector 106 [fig. 6].

In re claims 3 and 4, Anjan et al teach at column 3, lines 22-53 that the single mode or multimode optical fiber can be utilized as long as the formula is satisfied by

Application/Control Number: 10/543,288

Art Unit: 2874

the characteristics of the optical fiber utilized in the device.

In re claims 5 and 6, a star coupler 66 in fig. 4 is employed as the pitch and catch side optical routing device.

In re claim 20, it is clear that all the structural limitation near or in the catch side optical fiber inherently functions to minimize catch side mode noise.

In re claim 25, it is clear that all the structural limitation near or in the catch side alignment mechanism inherently functions to maximize the quantity of laser light coupled to the catch side optical fiber.

## Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

Application/Control Number: 10/543,288

Art Unit: 2874

Claims 9-13, and 26 are rejected under 35 U.S.C. 103(a) as being unpatentable over Anjan et al in view of Sappey et al [USPUB 20020181856].

Anjan et al discloses every aspect of claimed invention except for the multiplexer and the demultiplexer comprising an echelle grating.

Sappey et al show (de)multiplexer comprising an echelle grating.

It would have been obvious to the ordinary skilled person in the art at the time the invention was made to modify Anjan et al's device to include the multiplexer and the demultiplexer having the echelle grating as shown in Sappey et al for the purpose of enhanced efficiency in propagating optical signals [see Sappey et al's reference, column 2, ¶ 0012].

In re claim 11, Sappey et al show at column 3, ¶0038 that 1550 nm can be utilized.

In re claims 12 and 13, Sappey et al teach at column 2, ¶0010 that the select order is 4-7, the groove spacing can be 171.4 lines/nm, and the blaze angle can be 52.75 degrees.

In re claim 26, it is clear from the Sappey et al fig. 4, 6, 7 that the echelle grating is tilted along a first and second orthogonal axes.

In re claim 36, note that it has been held that a recitation with respect to the manner in which a claimed apparatus is intended to be employed does not differentiate the claimed apparatus from a prior art apparatus satisfying the claimed structural limitations. Ex parte Masham, 2 USPQ2d 1647 (1987).

## Allowable Subject Matter

Claims 7, 8, 14-19, 21-24, 27-31, and 32 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

The following is a statement of reasons for the indication of allowable subject matter: the prior art does not teach or fairly suggest a sensing apparatus and the method comprising all the specific elements with the specific combination including a data processing system determining a combustion parameter as set forth in claims 7, 34 and 45, including the optical coupler optically coupled to the distal end of the pitch side optical fiber and a distal end of an un-multiplexed input fiber as set forth in claim 14, including the means to mechanically manipulate by twisting the catch side multimode optical fiber around the longitudinal axis as set forth in claim 21, and including the means to tilt the catch optic comprising a stepper motor as set forth in claim 27.

## Conclusion

In formation regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR.

Page 6

Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

For all official patent application related correspondence for organizations reporting to the Commissioner of Patents:

Correspondence that is transmitted by facsimile must be directed to the central facsimile number, (703) 872-9306.

The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. Further references of interest are cited on Form PLO-892, which is attachment to this office action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Ellen Kim whose telephone number is (571) 272-2349. The examiner can normally be reached on Monday through Thursday. Mh

Ellen E. Kim

**Primary Examiner** 

August 30, 2006/EK